# ON THE RELAXATION MODULUS OF THE EQUIVOLUMINAL COMPOSITION OF SOLITHANE 113

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## INTRODUCTION

The purpose of this note is a comparison of the relaxation moduli of Solithane 50/50 (equivoluminal composition of Solithane 113) as determined from relaxation tests on ring specimen and strip specimen. Ring specimen are a particularly convenient type of specimen for testing the mechanical properties of elastomers under uniaxial tension. However, the lack of an accurate analysis of the stresses and strains in this geometry complicates the definition of the true stress and strain in the ring test sections and may lead to incorrect data reduction.

New data on the relaxation modulus of Solithane 50/50 has been obtained from tests on strip specimen and is compared to the data which has earlier been obtained with ring specimen [1]. The two schemes employed for reducing both sets of experimental data are briefly described. The particular ring geometry used in these experiments is found to be unsuited for relaxation tests at small strains.

### TESTS WITH STRIP SPECIMEN

Strips of 0.5 in width were cut out of a cast sheet of Solithane 50/50. The sheet had a thickness of 0.1 in and could be easily cut with the help of a razor blade. Metal tabs were then glued on either end of the strips leaving a straight test section of 4 in length in between them. Figure 1 shows the test specimen. No special precautions were necessary to avoid fracture at the ends of the test section because the relaxation tests were carried out at less than 3% strain.

The effect of the metal tabs on the stress and strain field was neglected and the two quantities were calculated as follows

$$\varepsilon = \frac{\Delta 1}{1}, \qquad (1a)$$

$$\sigma = \frac{F}{A_o}, \qquad (1b)$$

where

1 = length of specimen test section,

 $\Delta l_i^{j}$  = increase in the length of the test section,

F = force,

A = cross section of the unstretched specimen,

σ = engineering stress.

The tests were carried out with the help of an Instron tester. The constant strain  $\epsilon_0$  cannot be obtained in a truly step wise manner in practice and a ramp strain history as shown in Figure 2 is employed. A strain rate of 0.5 min<sup>-1</sup> was used in order to avoid the overshoot encountered at higher Instron crosshead speeds when the crosshead motion is stopped. The rise time necessary to reach the constant strain  $\epsilon_0 = 0.025$  is equal to  $t_0 = 0.05$  min in this case.

Assuming the material to behave linearly viscoelastic [2], the stress as a function of time is equal to

$$\sigma(t) = R \int_{0}^{t} E_{rel}(\tau) dt \qquad \text{for} \qquad 0 \le t \le t_{o}, \qquad (2a)$$

$$\sigma(t) = \frac{\varepsilon_0}{t_0} \int_{t-t_0}^{t} E_{rel}(\tau) dt \quad \text{for} \quad t > t_0, \quad (2b)$$

where 
$$R = \frac{\epsilon_0}{t_0} = \text{strain rate,}$$

E<sub>rel</sub> = relaxation modulus,

t<sub>o</sub> = rise time.

The stress  $\sigma(t)$  as a function of time is readily obtained from the force history recorded on the Instron chart and equation (1b). Equations (2a) or (2b) are then strictly speaking integral equations for the relaxation modulus. The second of these equations may, however, be approximated by

$$\sigma(t) \approx \frac{\epsilon_{o}}{t_{o}} \quad t_{o} \quad E_{rel}\left(t - \frac{t_{o}}{2}\right) \tag{3}$$

thus leading to a direct relationship between stress history and relaxation modulus

$$E_{rel}(t) \approx \frac{\sigma \left(t + \frac{t_o}{2}\right)}{\epsilon_o}$$
 ,  $t > t_o$  (4)

The geometrical interpretation of the approximation is shown in Figure 3. For times  $t \gg t_0$  the argument of the stress in equation (4) can simply be replaced by t.

The results of relaxation tests carried out in this manner at various temperatures are presented in Figure 4. The segments of the relaxation modulus show the typical time and temperature dependence and can be easily shifted into a single relaxation curve. This curve is shown in Figure 5 for a reference temperature of 0°C. The previously determined time-temperature shift factor between 0°C and -5°C has been used to refer the data to 0°C although -5°C was the lowest temperature at which tests were run in this test series.

#### TESTS WITH RING SPECIMEN

The results of the tests with ring specimen have already been presented in reference 1. Only a brief description of these tests and of the data reduction will be given here in order to facilitate a comparison with the new data.

The ring specimen were cut out of cast Solithane 50/50 sheets of 0.1 in thickness by means of a rotating cutting tool. The cut surfaces were not of the same high quality as the surfaces of the cast sheet or as of cuts made with a razor blade. Each specimen was visually inspected and faulty specimen were singled out. The inner and outer diameter of each ring were about 0.65 in and 0.75 in, respectively. They were individually measured for each ring with the help of an optical comparator. Figure 6a shows a ring in its undeformed state.

For testing, a ring was put over two stainless steel pins of 0.378 in diameter. These pins were attached to the Instron crosshead and load cell, respectively. The initial distance  $l_d$  between the pin centers was such that the fiber at the ring inside remained unstretched after placing the ring over the pins. Figure 6b shows the ring in this condition. The two straight segments of length  $l_d$  are considered the test sections of the ring. As the distance between the pin centers is increased by some  $\Delta l$  these test sections are stretched and are essentially in a state of uniaxial tension if the stresses introduced by bending the originally round ring into this shape and the end affects near the pin can be neglected. This may with some confidence be assumed when the ring is thin, that is

$$1 - \frac{D_i}{D_0} << 1$$

and when the distance between the pin centers is large compared to the pin diameter d. The inner and outer diameter of the original ring are denoted by  $D_i$  and  $D_o$ , respectively. The diameter of the pins has to be large enough, however, to not introduce too large bending stresses in the stretched ring which could lead to premature failure.

The average stress in the two ring test sections is simply defined as

$$\sigma = \frac{F}{2A_n} \tag{5}$$

where  $A_r = ring cross section$ .

Several definitions of the strain in these ring segments are possible. An accurate stress-strain analysis of this difficult geometry is not available and the strain is often based on the original length of some ring fiber. In terms of the central fiber one arrives at the following measure

$$\varepsilon = \frac{4 \Delta 1}{\pi \left(D_1 + D_0\right)} \tag{6}$$

A simple analysis of the stresses and strains in the stretched ring by Blatz [3] leads to the following expression for the average strain across the ring

$$\epsilon_{cr} = \frac{1}{\sqrt{1 + \frac{2\Delta 1}{C_{io}}}} + \frac{1 + \frac{2\Delta 1}{C_{io}}}{\sqrt{1 + \frac{2\Delta 1}{C_{io}}}} - 1$$
 (7)

where 
$$S_o = \frac{2\pi}{C_{io}} \left( \frac{D_i + D_o}{2} - \frac{d}{2} \right)$$

$$C_{io} = 2 l_d + \pi d.$$

For the values of d,  $D_i$ ,  $D_o$ , and  $1_d$  mentioned earlier this relationship gives a value for the average strain that differs only very little from the one given by equation (6). Figure 7 shows the comparison of the two values as a function of  $\Delta l$  and some other strain definitions.

Definitions (5) and (6) were used to reduce the relaxation data obtained by testing the ring specimen. The strain history and the calculation of the relaxation modulus are the same as described for the strip specimen. The relaxation modulus arrived at in this manner is shown in Figure 8. The strain at which this modulus has been determined is  $\epsilon_0 = 0.05$ .

## COMPARISON OF THE DATA

Figure 8 shows the relaxation moduli obtained by testing ring specimen and strip specimen. Solithane 50/50 may be considered linearly viscoelastic up to about 7% strain and the different strains  $\epsilon_0$  for which these moduli have been obtained do not affect the result. The relaxation modulus calculated from experiments with strip specimen is seen to be higher at short times than the modulus derived from the experimental data for the ring specimen. In both cases the specimen reaches its long time equilibrium at  $0^{\circ}$ C after about 1 minute and the rubbery modulus  $E_r$  is the same for both sets of data.

The discrepancy at short times is too large to be entirely caused by batch to batch variations in material properties. It is believed to be caused by the non-uniformity of the stress and strain fields in the ring specimen. The test sections of the ring are seen to be relatively short compared to the pin diameter and the circumference of the ring, cf. Figures 6a,b. The non-uniformity seems to make the simple definition of stress (5) and strain (6) in the ring the more unrealistic the higher the modulus of the ring material is, i.e., lower temperatures or shorter times.

It must be concluded from Figure 8 that for the small strains employed in stress relaxation tests the ring size is too small in comparison to the pin dimensions to obtain reliable results with the simple definitions of stress and strain (5,6). An adequate stress-strain analysis of this geometry, however, which could lead to a more realistic interpretation of the experimental data is not yet available.

Figure 9 shows the time-temperature shift factors obtained by shifting both sets of data. The temperature dependence and magnitude of the shift factor is seen to be the same in both cases except for the lowest temperatures at which tests were run.

## REFERENCES

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- 3. Blatz, P. J.; George, N.; Ko, W. L.; Murthy, A.; Yoh, J., "Physicomechanical Behavior of Rubberlike Materials", MATSCIT PS 64-8, California Institute of Technology, Pasadena, California (1964).

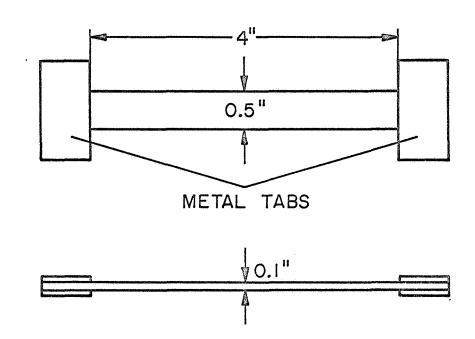


Fig. I STRIP SPECIMEN

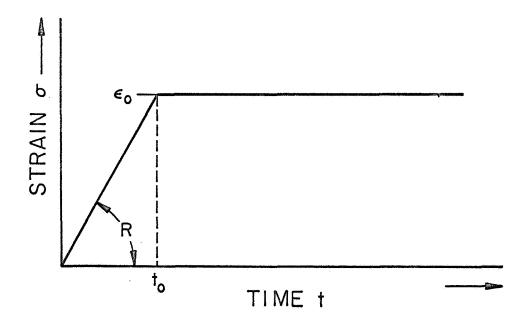


Fig. 2 STRAIN HISTORY

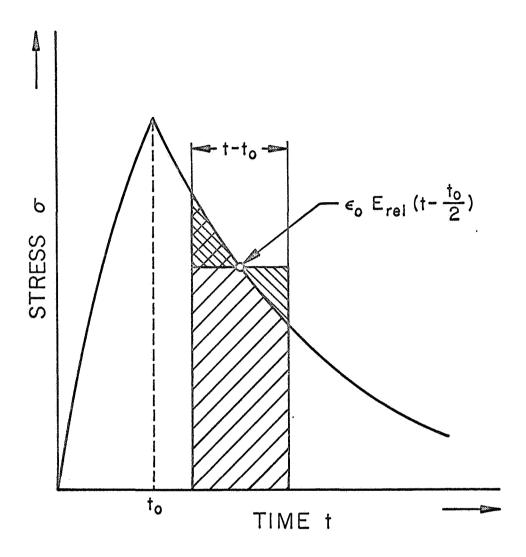
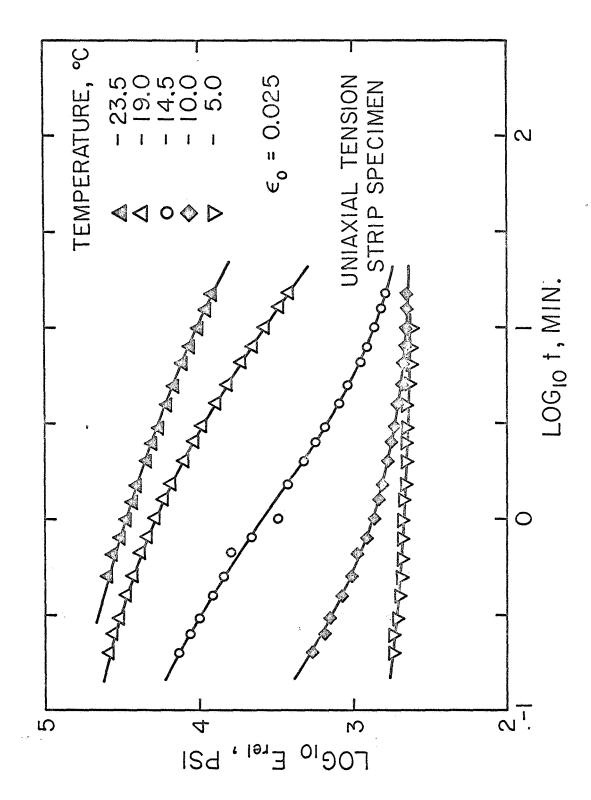


Fig. 3 GEOMETRICAL INTERPRETATION OF EQUATION 4.



RELAXATION MODULUS OF SOLITHANE 50/50. Fig. 4

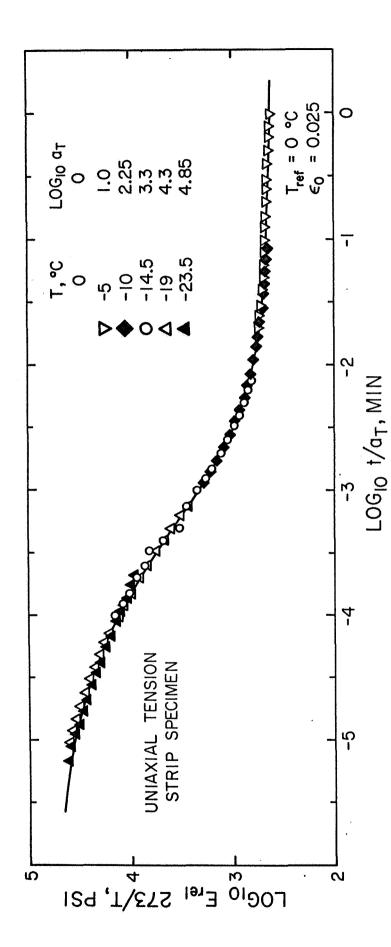


Fig. 5 RELAXATION MODULUS OF SOLITHANE 50/50.

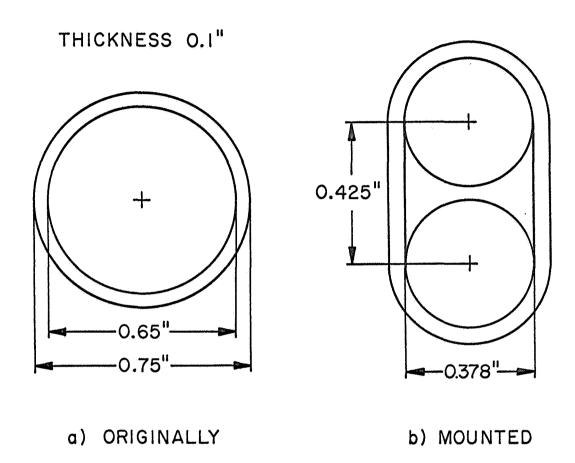


Fig. 6 RING SPECIMEN

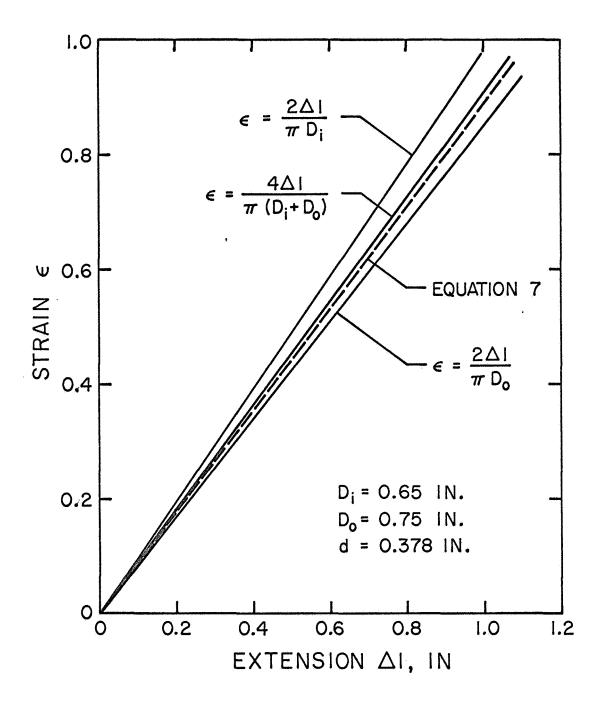


Fig. 7 COMPARISON OF VARIOUS STRAIN DEFINITIONS FOR THE RING SHOWN IN Fig. 6.

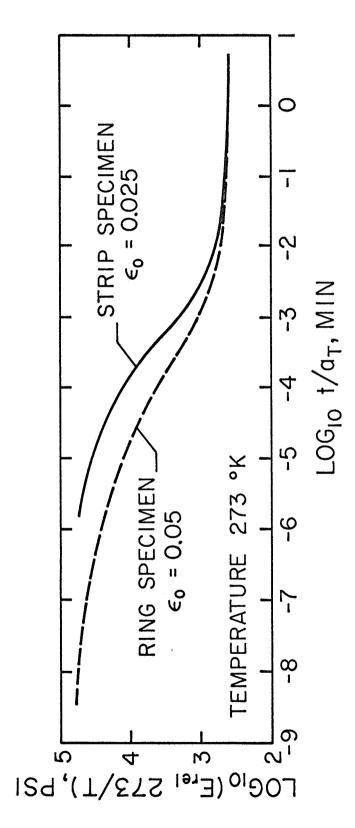


Fig. 8 COMPARISON OF RELAXATION MODULI FOR SOLITHANE 50/50.

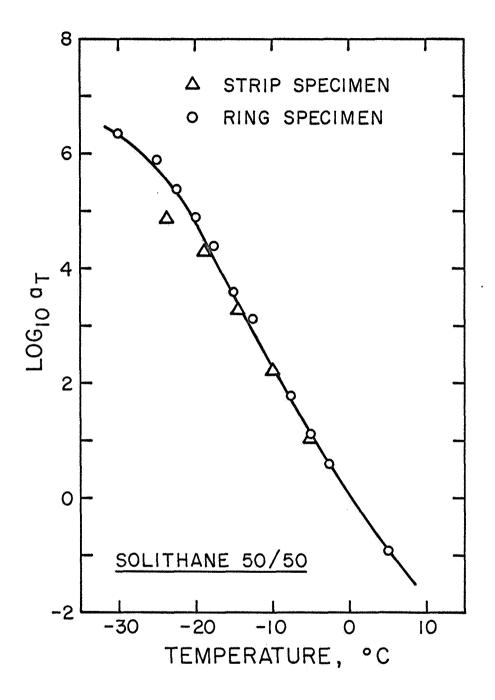


Fig. 9 COMPARISON OF THE TIME-TEMPERATURE SHIFT FACTOR FOR THE TWO SETS OF DATA.